

Computer Simulations of Surfactant Self-Assembly

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In this letter we present the results of computer simulations of a simple water/surfactant model, from which we obtained a complete micellar size distribution. We are able to observe (equilibrium) dynamical processes such as the entering of single surfactants into micelles, single surfactants leaving micelles, the fusion of two micelles, and the slow breakdown of a micelle. We use our results to answer some controversial questions concerning the interactions that are essential for surfactant self-assembly.

The dynamics of self-assembled surfactant structures are of importance in a variety of processes ranging from the transport of molecules through cell membranes to the removal of stains in a washing machine. Even in the simplest assemblies, micelles in water, the time scales of dynamical processes may vary from 10^{-8} to 10^{-2} s. Here we present the results of molecular dynamics simulations of a simple surfactant/water model. Together with the equilibrium properties, these simulations yield the dynamical processes that are observed experimentally.

In computer simulations on "realistic" models of surfactants the assembly is constructed a priori and this structure is studied for several tenths of a nanosecond.¹⁻⁴ These simulations yielded important information about the structure of the aggregate. However, the study of the dynamics is limited to only very short time scales.⁵ Furthermore, it is clearly impossible to study the collective behaviour of several assemblies using these models. This collective behavior turns out to be essential in the dynamics of micelles. An alternative approach, using simplified models, shows the spontaneous formation of monolayers, micelles,^{6,7} and also a membrane.⁸ An intriguing question is whether it is possible to observe in a computer simulation of a simple molecular model the dynamics that is observed experimentally in these systems.⁹ That this is far from obvious becomes clear if we recall that even in the simplest case, micelles in water, the relevant time scales range from 10^{-8} s, which is the time it takes a surfactant to leave or enter a micelle, to 10^{-2} s, the time scale of the fusion of micelles.

In our model, two simple observations¹⁰ constituted our starting point: oil and water do not mix, and a surfactant is an amphiphilic molecule, i.e., a molecule of which one side is hydrophilic and dislikes oil and the other side is hydrophobic and likes oil.

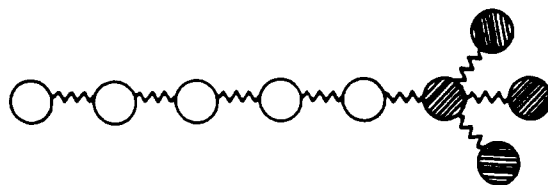


Figure 1. A schematic drawing of the surfactant structure. In our model we distinguish w particles to model water (not shown), h particles to model the head segments of a surfactant (shaded spheres), and t particles for the tail segments (open spheres).

We assume the existence of three types of particles: w particles, h particles, and t particles. These particles are used to model two types of molecules, namely, water molecules and surfactant molecules. A water molecule consists of a single w particle. A surfactant molecule is made up of t particles and h particles, joined by harmonic potentials. The particles interact with truncated and shifted Lennard-Jones potentials with energy parameter ϵ_{ij} , distance parameter σ_{ij} , and the cut-off radius R_{ij}^c . We have assumed that for all interactions $\epsilon_{ij} = \epsilon$ and $\sigma_{ij} = \sigma$. In order to make the interactions different, the truncation of the potential (R_{ij}^c) is made depending on the type of interaction. The w-w, w-h, and t-t interactions are truncated at $R_{ij}^c = 2.5\sigma$ and the w-t, h-h, and t-h interaction at $R_{ij}^c = 2^{1/6}\sigma$, which makes the latter interactions completely repulsive. The surfactant structure is shown in Figure 1.

The simulations were performed at constant temperature ($T = 2.2\epsilon/k_B$) and density ($\rho = 0.7\sigma^{-3}$) with 32 000 particles. The simulations were started with a random distribution of surfactants and were continued for more than 10^6 time steps ($\Delta t = 0.005\tau_0$ ($\tau_0 = \sigma(m/\epsilon)^{1/2}$)). These simulations were run on a network of 400 transputers using the same parallel molecular dynamics algorithm as in ref 7.

Figure 2 shows a snapshot of a part of our system as obtained from a molecular dynamics simulation. It clearly demonstrates that surfactant clusters are formed. An important point is, however, that one snapshot does not contain sufficient information to characterize a micellar solution. A solution containing micelles can be described quantitatively by the size distribution of aggregates.¹¹ We can determine this distribution by counting the clusters at regular intervals. The obtained equilibrium cluster distribution function shown in Figure 3 has an optimum cluster size of 22 to 23 surfactants. We observe micelles with sizes ranging from 15 to 30 surfactants, indicating a significant polydispersity. An important aspect is that in

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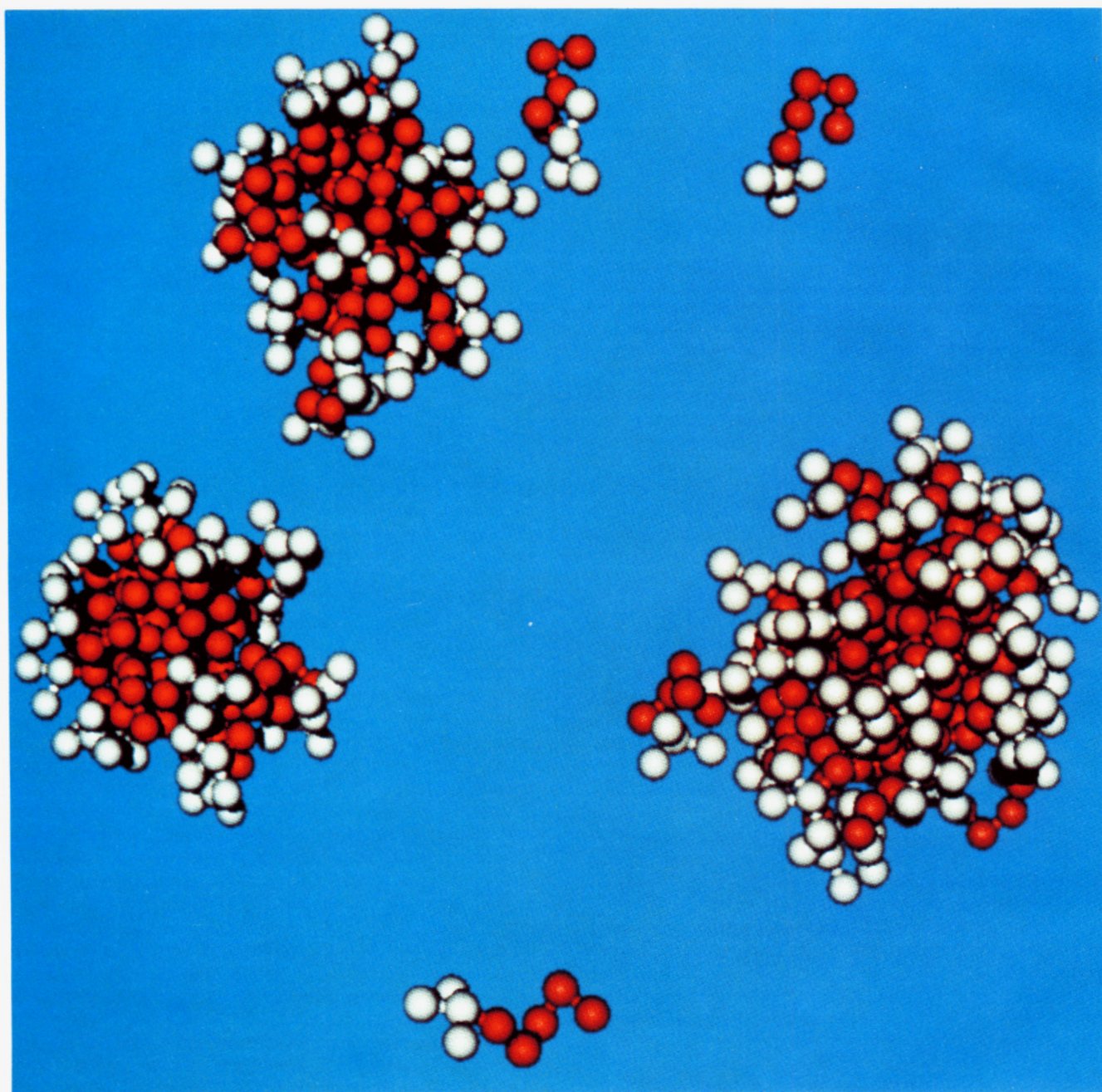


Figure 2. Snapshot of a small part of the system. For clarity only the surfactants are shown; the white spheres are the hydrophilic segments, the red spheres the hydrophobic.

the distribution function we observed a maximum and a minimum between the (proper) micelles and the oligomers. Such a shape of the distribution function has been predicted by various mass-action models¹² and is one of the basic assumptions in the theory of the dynamics of micelle formation.⁹ Our results demonstrate that a simple molecular surfactant/water model gives rise to such a distribution. It is generally believed that a micelle size distribution should have a shape like the one presented in Figure 3, but the complete curve cannot be measured experimentally. Therefore, as far as we know, our computer simulations are the first to confirm these basic theories.

Having established that our model shows the same behavior as an equilibrium micellar solution, we can now

study the dynamics. In our simulations we observe that monomers leave a micelle and enter another micelle, that two micelles fuse, and occasionally that a micelle that looks initially stable falls apart. To obtain a quantitative description of these phenomena, it is useful to look at the evolution of typical micelles and of some individual surfactants. This is shown in Figure 4. In Figure 4a the size evolution of a micelle, with roughly an optimum number of surfactants, is shown. The micelle shows small fluctuations in size when an individual surfactant leaves or enters a micelle, but nothing dramatic happens. A different behavior is observed when we follow two micelles which have a size which is not optimum as is shown in Figure 4b. These two micelles fuse and form one big micelle. According to Figure 3 it can be expected that this big micelle is not very stable, which is reflected in Figure 4b since its size rapidly decreases toward a more optimum

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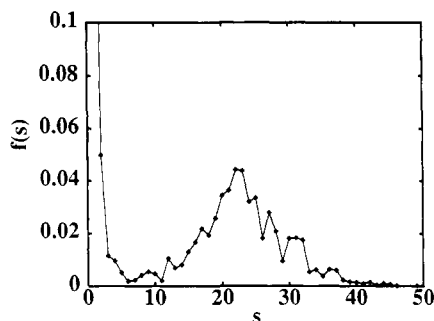


Figure 3. Micellar size distribution function $f(s)$. s is the number of surfactants in an aggregate. The figure has been obtained by averaging over approximately 200 configurations taken every 4000th time step and normalized by dividing by the total number of clusters. In order to check the reliability of this curve, we prepared a system with an entirely different initial configuration at a much lower temperature. At this configuration all surfactants were in aggregates. The temperature was then increased to $T = 2.2\epsilon/k_B$, and after equilibration the obtained micellar distribution function was indistinguishable from the one obtained starting from a completely random distribution of surfactants. An estimate of the critical micelle concentration can be obtained from $f(1)$.

micellar size. Furthermore, we see occasionally (not shown) the complete breakdown of a micelle, which is a much slower process than the leaving or entering of a single surfactant. These dynamical processes are exactly what is observed experimentally in systems with strongly screened electrostatic interactions,⁹ to which our model closely corresponds. The simplicity of our model allows us to use a larger time step, requires less cpu time, and has a faster intrinsic dynamics than simulations of realistic models.¹⁻⁴ As a result the relevant dynamical processes in this model occur on a time scale accessible to a simulation.

The molecular interactions that play an essential role in promoting surfactant self-assembly are still the subject of debate. For a long time the general belief was that aggregation is driven by the unique properties of water,¹³ until experiments showed that micelle formation also occurred in other liquids.¹⁴ Beesly et al.¹⁵ concluded from an experimental survey that for cooperative interaction between amphiphilic molecules, hydrogen bonding is essential. In our model there are no explicit hydrogen bonds. Therefore, in contrast to the suggestions in the literature, our simulations show that hydrogen bonds are *not* essential for the formation of micelles. Furthermore, in our model the interactions between head groups is short-ranged repulsive, and it is therefore not essential to have *long-ranged* repulsive interactions for the formation of

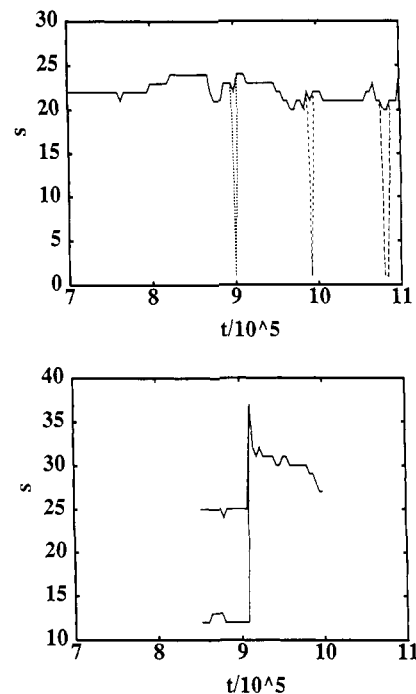


Figure 4. Evolution of micelles; the full line shows the total number of surfactants (s) in these micelles as a function of time t (in a particular time interval). In part a (top) the micelle shows small size fluctuations around its average value, caused by the entering or leaving of a single surfactant. The broken lines show the evolution of three single surfactants belonging to this micelle. Part b (bottom) shows the fusion of two aggregates into one large micelle (note that the origin has been shifted).

micelles, as is suggested in ref 16. Our conclusions are in line with the results from lattice models of surfactant systems.^{10,17,18}

In summary, in this letter we have presented the results of molecular dynamics simulations of a simple water/surfactant system. Whereas previous simulations were limited to one micelle, our simulations yielded a complete equilibrium micellar size distribution function. The results show that by using a simple model, computer simulations can be used to study dynamical processes with time scales that span as much as 6 decades experimentally. We feel that it is remarkable and above all encouraging to see that an interaction model as simple as the one presented here is capable of yielding such a reasonable description of these complex systems.

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